

STIC-FPAS

From: Wilson, Donald
Sent: Monday, June 09, 2003 7:32 AM
To: STIC-FPAS
Subject: Translation Request

PTO 2003-3895

S.T.I.C. Translations Branch

Translation Requester Information:

Requester's Name: **Don Wilson**

U.S. Serial Number: **10/037,543**

Telephone Number: 703-308-2398

Office Location: CP3/4E-08

Art Unit or Organization Name: 1713

Is this for the Board of Patent Appeals?: NO

Date needed by (please BE SPECIFIC): 8/9/03

Document Identification (Select One):

Patent:

Document Number: 44-32054 B4

Country Code: JP

Publication Date: 12/20/1969

Language: Japanese

Article:

Author:

Language:

Country:

Other:

Type of Document:

Language:

Country:

22 KHU Copy E-Mail 6-25-03

To assist us in providing the most cost-effective service, please answer these questions:

Will you accept an English Language Equivalent (Yes/No)? Yes

Copy/Search

Processor: GP

Date Assigned: 6-9-03

Date filled: 6-9-03

Equivalent found (Y/N): NO

Doc. No.: _____

Country: _____

Translation: 6.9.03

Date logged in: 7-14-03

PTO est. words: _____

No. of pages: _____

In-house trans. avail: _____

In-House: _____

Translator: _____

Assigned: _____

Returned: _____

Contractor: _____

Name: mc

Priority: 6-19-03

Sent: 6-25-03

Returned: 6-25-03

RECEIVED
2003 JUN -9 PM 2:43
TRANSLATIONS DIVISION
USPTO SCIENTIFIC LIBRARY

Would you like to review this document with a translator prior to having a complete written translation (Yes/No)? Already have.

(Translator will contact you to set up a mutually convenient time.)

Would you like a Human Assisted Machine Translation (Yes/No)? Not available.

(Human Assisted Machine Translation provided by Derwent/Schreiber is the default for Japanese patents from 1993 onwards, with an average 5-day turnaround.)

Copy/Search
Processor: _____
Date Assigned: _____
Date filled: _____
Equivalent found (Y/N): _____
Doc. No.: _____
Country: _____

Translation:
Date logged in: _____
PTO est. words: _____
No. of pages: _____
In-house trans. avail: _____

In-House: _____	Contractor: _____
Translator: _____	Name: _____
Assigned: _____	Priority: _____
Returned: _____	Sent: _____
	Returned: _____

PTO 03-3895

Japanese Kokoku Patent No.
Sho 44[1969]-32054

METHOD FOR PRODUCING STABILIZERS FOR POLYOLEFINS

Kazuo Nakatsuka, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. JUNE 2003
TRANSLATED BY THE RALPH MCELROY TRANSLATION COMPANY

JAPANESE PATENT OFFICE
PATENT JOURNAL
KOKOKU PATENT NO. SHO 44[1969]-32054

Japanese Cl.:	26 B 151 25 H 05 26 B 121 26 B 11 25 H 31 13 C 1
Filing No.:	Sho 40[1965]-81631
Filing Date:	December 30, 1965
Publication Date:	December 20, 1969
No. of Inventions:	1 (Total of 5 pages)

METHOD FOR PRODUCING STABILIZERS FOR POLYOLEFINS

[Poriorefinyo anteizaino seizohoho]

Inventors:	Kazuo Nakatsuka, et al.
Applicant:	Mitsubishi Rayon Co., Ltd.

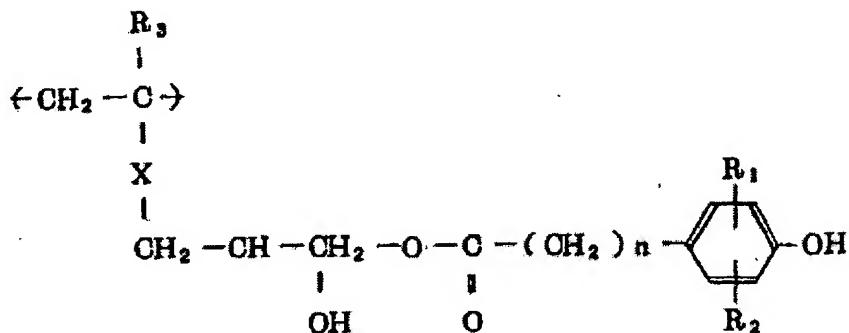
[There are no amendments to this patent.]

Detailed explanation of invention

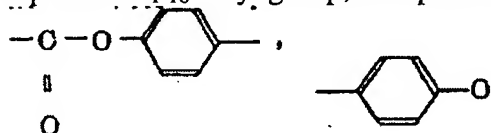
The present invention relates to a method for producing new stabilizers effective for prevention of oxidative degradation of polyolefins, especially polypropylene.

Noticing that most stabilizers on the market for polyolefins had a fatal drawback that those stabilizers were dispersed and leached from polyolefin molded materials by various treatments and the permanent stability of the molded materials could not be secured, the present inventors assiduously conducted a study for the development of an effective stabilizer, which is little dispersed and leached, especially from polyolefin molded materials, and, as a result, a new stabilizer containing phenol groups was found.

Namely, it was found that an addition polymer containing phenol groups is extremely effective having a constituent unit expressed by the general formula:

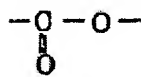


wherein R_3 represents hydrogen or methyl group; one of R_1 and R_2 represents hydrogen or both represent C_{1-18} alkyl group; X represents



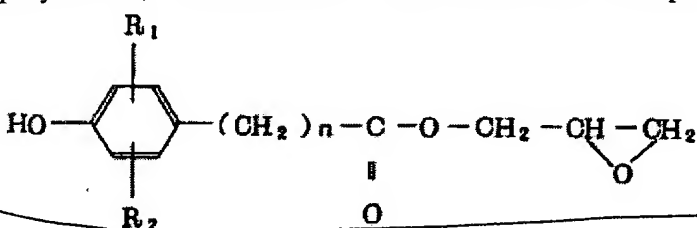
or $-CH_2O-$; n represents an integer of 0, 1, 2, 3), and a patent application was filed for it.

However, a study on the industrial production method for the stabilizer especially with



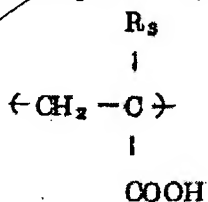
as X was further continued to complete the synthetic process of the present invention.

Namely, the purport of the present invention is a method for producing stabilizers for polyolefins, characterized in that at least one of compounds having the general formula:



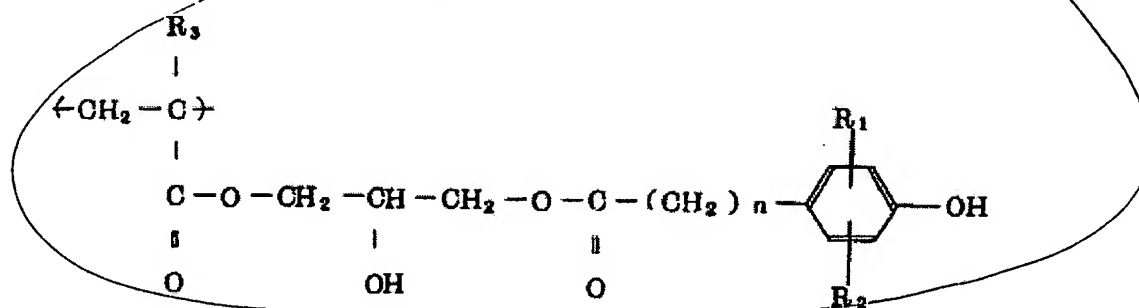
(I)

(in the formula, one of R_1 and R_2 represents hydrogen or both represent C_{1-18} alkyl group; n represents an integer of 0, 1, 2, 3) is reacted with a polymer or copolymer having a constituent unit expressed by the general formula:



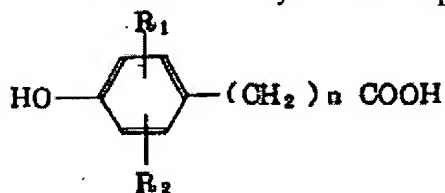
(II)

(in the formula, R_3 represents hydrogen or methyl group) to obtain an addition polymer having the constituent unit expressed by:



(in the formula, R_1 , R_2 , R_3 and n are same as in the aforementioned general formulas (I) and (II)). According to the production method of the present invention, the aforementioned phenol group-containing addition polymer effective as a stabilizer for polyolefins, especially polypropylene, can be simply obtained.

As detailed examples of compounds expressed by the general formula (I) which are one of the starting materials in the present invention, there are glycidyl 3-tert-butyl-4-hydroxybenzoate, glycidyl 3,5-di-tert-butyl-4-hydroxybenzoate, glycidyl 3-tert-butyl-6-methyl-4-hydroxybenzoate, glycidyl 3-tert-octyl-5-methyl-4-hydroxybenzoate, glycidyl 3-tert-butyl-5-ethyl-4-hydroxybenzoate, glycidyl 2-(3-tert-butyl-4-hydroxyphenyl)acetate, glycidyl 2-(3,5-di-tert-butyl-4-hydroxyphenyl)acetate, glycidyl 2-(3-tert-butyl-6-methyl-4-hydroxyphenyl)acetate, glycidyl 2-(3-tert-butyl-5-ethyl-4-hydroxyphenyl)acetate, glycidyl 2-(3-tert-octyl-5-methyl-4-hydroxyphenyl)acetate, glycidyl 3-(3-tert-butyl-4-hydroxyphenyl)propionate, glycidyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, glycidyl 3-(3-tert-butyl-6-methyl-4-hydroxyphenyl)propionate, glycidyl 3-(3-tert-butyl-5-ethyl-4-hydroxyphenyl)propionate, glycidyl 3-(3-tert-octyl-5-methyl-4-hydroxyphenyl)propionate, glycidyl 4-(3-tert-butyl-4-hydroxyphenyl)butyrate, glycidyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)butyrate, glycidyl 4-(3-tert-butyl-6-methyl-4-hydroxyphenyl)butyrate, glycidyl 4-(3-tert-butyl-5-ethyl-4-hydroxyphenyl)butyrate, glycidyl 4-(3-tert-octyl-5-methyl-4-hydroxyphenyl)butyrate, etc., and all of these compounds can be easily synthesized from carboxylic acids expressed by the general formula:



(in the formula, R_1 , R_2 and n are same as in the general formula (I)),

and epichlorohydrin.

The other starting material in the present invention is a polymer or copolymer having the constituent unit expressed by the general formula (II), and as detailed examples there are methacrylic acid polymer, acrylic acid/styrene copolymer, acrylic acid/methyl acrylate copolymer, methacrylic acid/methyl acrylate copolymer, acrylic acid/vinyl acetate copolymer, methacrylic acid/vinyl acetate copolymer, acrylic acid/ethylene copolymer, methacrylic acid/ethylene copolymer, etc. The aforementioned polymer or copolymer is easily obtained from corresponding monomers by known methods, for example, polymerizing using radical polymerization initiators, light or heat, etc. As the average polymerization degree of the polymer or copolymer, 1000 or less is desired in consideration of antioxidation effect of polypropylene, and it can be easily achieved by using a suitable amount of a chain-controlling agent such as mercaptan, etc.

The production method of the present invention is to react the aforementioned two starting materials, namely, at least one compound expressed by the general formula (I) and the polymer or copolymer having the constituent unit expressed by the general formula (II). As the reaction conditions in this case, the reaction of the starting materials is easily advanced only by heating in the absence of solvent or the presence of a solvent such as tetrachloroethane, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, etc., or in a polyolefin such as polypropylene, etc., at a temperature of 100-300°C to obtain a phenol group-containing addition polymer having the constituent unit expressed by the general formula (III).

The stabilizer thus obtained, namely, the aforementioned phenol group-containing addition polymer having the constituent unit expressed by the general formula (III), reveals an excellent efficiency as a permanent stabilizer for polyolefins, and actually polyolefins can be stabilized at a concentration of 0.01-20 wt% (vs. polyolefin). Furthermore, when it is used together with a known peroxide [anti]-decomposition agent or a UV absorbent, etc., the stabilization of polyolefins can be increased by synergic action.

As explained above, the aforementioned phenol group-containing addition polymer especially effective as a stabilizer for polyolefins, particularly polypropylene, can be easily obtained by the production method of the present invention, and the arrival of the present invention will greatly contribute to the development of this industry.

Further, organic macromolecular compounds such as polyamide, polyvinyl chloride, acrylic resin, ABS resin, styrene resin, etc., in addition to polyolefins, can be stabilized by the addition polymer.

Hereinafter, the present invention is explained in detail by application examples.

"Parts" in the examples means parts by weight.

Application Example 1

Sodium 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate 100 parts, epichlorohydrin 300 parts and tetramethylammonium iodide 2.6 parts were heated at 80°C for 3 h under stirring, and after completing the reaction the mixture was washed with water and vacuum distilled to obtain 58 parts of glycidyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (boiling point 197-212/3 mmHg).

Next, 33 parts of the aforementioned glycidyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate and 19 parts of methacrylic acid/styrene copolymer (weight ratio: 45/55) having average molecular weight of 5200 were dissolved in 100 parts dimethyl sulfoxide and reacted 5 h at 140°C. After completing the reaction, the reaction mixture was cooled to room temperature, and a water/methanol mixture was added to the reaction mixture to precipitate the addition polymer. It was washed with water/methanol and dried to obtain an addition polymer, 49 parts in yield. According to the infrared absorption spectra, the absorption at wave number 910 cm^{-1} based on epoxy group disappeared and the absorption of hydroxyl group at 3500 cm^{-1} was confirmed. Thus, it was confirmed from the above results that an addition polymer of an epoxy group and carboxylic group was produced.

Application Example 2

Acrylic acid/ethylene copolymer (weight ratio: 10/90) with 12000 average molecular weight 72 parts and glycidyl 3-(3-tert-octyl-5-methyl-4-hydroxyphenyl)propionate 35 parts were reacted 30 min at 200°C. The addition polymer thus obtained was pulverized and extracted with methanol to remove unreacted epoxy compound, and the infrared spectrum of the residue was recorded to confirm phenyl group-based absorption.

Application Example 3

Acrylic acid/methyl methacrylate copolymer (weight ratio: 50/50) with 4500 average molecular weight 1.4 parts, glycidyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate 3.4 parts and polypropylene powder 45.2 parts were mixed and kneaded at 220°C for 20 min. A film was formed from the polymer thus obtained and the infrared spectrum was recorded. The absorption of epoxy group at wave number 910 cm^{-1} disappeared and the absorption of hydroxyl group at 3500 cm^{-1} was newly confirmed. Thus, it was confirmed from the above results that an addition polymer of an epoxy group and carboxylic group was produced.

Practical example

(A): A polypropylene powder of intrinsic viscosity 1.5 was mixed with 1.0 wt% of the phenol group-containing addition polymer obtained in Application Example 1, molded at 220°C,

melt spun at 270°C, and drawn at 130°C to obtain a untreated yarn. Further, the yarn was treated in tetrachloroethylene at a bath ratio of 1:50 and 32°C for 20 min to obtain a dry cleaning-treated yarn.

(B): Polypropylene containing the phenol-containing addition polymer obtained in Application Example 3 was diluted to 10x using unmodified polypropylene, and from it an untreated yarn and a dry cleaning-treated yarn were obtained by the same manner as above.

(C): Polypropylene powder was mixed with 0.3 wt% of Ionol (2,6-di-tert-butyl-4-methylphenol) as a known stabilizer, instead of the aforementioned stabilizer, and in the same manner an untreated yarn and a dry cleaning-treated yarn were obtained.

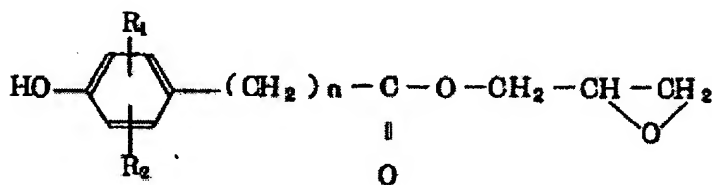
Next, an accelerated degradation test was conducted on these samples in a hot air dryer at 140°C to determine the degradation initiation time (h) as shown in the following table.

Sample Number	Untreated yarn	Dry cleaning-treated yarn
(A)	92	84
(B)	78	70
(C)	52	8
without stabilizer	2	2

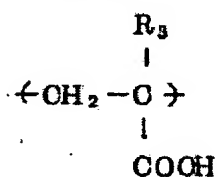
It was clearly confirmed by the above results that the stabilizers (A) and (B) prepared by the production method of the present invention are superior compared to conventional stabilizers in giving polypropylene permanent stability.

Claim

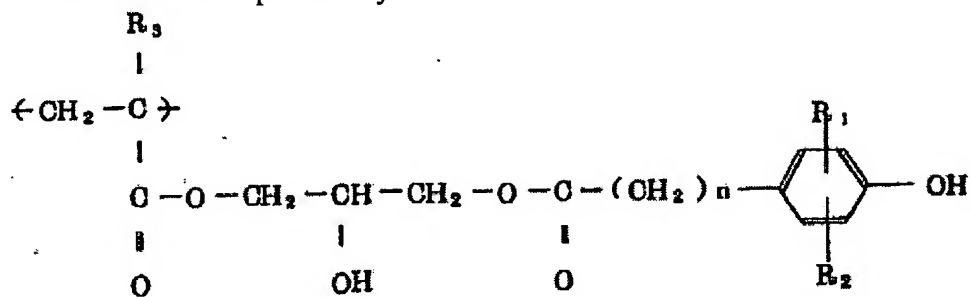
1. A method for producing stabilizers, characterized in that at least one compound having the general formula:



(in the formula, one of R₁ and R₂ represent hydrogen or both represent C₁₋₁₈ alkyl group; n represents an integer of 0, 1, 2, 3) is reacted with a polymer or copolymer having a constituent unit expressed by the general formula:



(in the formula, R_3 represents hydrogen or methyl group) to obtain an addition polymer having the constituent unit expressed by:



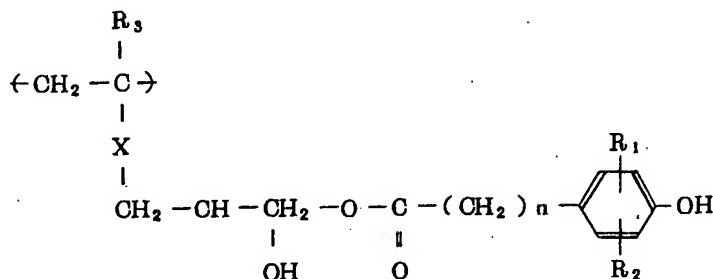
(in the formula, R_1 , R_2 , R_3 and n are same as in the aforementioned general formulas).

(全5頁)

2

* 代理人 弁理士 田村武敏

代 表 者 清水喜三郎

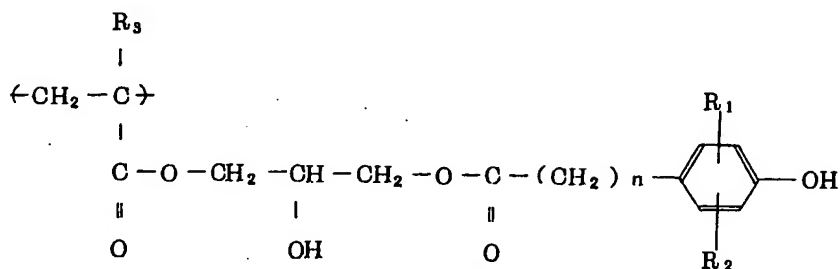


2, 3の整数)で示される構成単位を有するフェノール基含有付加重合体が極めて有効であることを見出し、既に「ポリオレフィン組成物」として 35 特許出願中であるが、その後更に該安定剤のうち特にXが $-O-O-$ のもの工業的な製造方法に

WEST



10

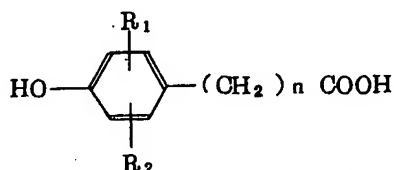


酸グリシジル、2-(3-第3級ブチル-5-エチル-4-ヒドロキシフェニル)酢酸グリシジル、2-(3-第3級オクチル-5-メチル-4-ヒドロキシフェニル)酢酸グリシジル、3-(3-第3級ブチル-4-ヒドロキシフェニル)プロピオン酸グリシジル、3-(3,5-ジ第3級ブチル-4-ヒドロキシフェニル)プロピオン酸グリシジル、3-(3-第3級ブチル-6-メチル-4-ヒドロキシフェニル)プロピオン酸グリシジル、3-(3-第3級ブチル-5-エチル-4-ヒドロキシフェニル)プロピオン酸グリシジル、3-(3-第3級オクチル-5-メチル-4-ヒドロキシフェニル)プロピオン酸グリシジル、4-(3-第3級ブチル-4-ヒドロキシフェニル)酪酸グリシジル、4-(3,5-ジ第3級ブチル-4-ヒドロキシフェニル)酪酸グリシジル、4-(3-第3級ブチル-6-メチル-4-ヒドロキシフェニル)酪酸グリシジル、4-(3-第3級ブチル-5-エチル-4-ヒドロキシフェニル)酪酸グリシジル、4-(3-第3級オクチル-5-

本発明の出発物質の一つである一般式(I)で示される化合物とは、具体的には、例えば3-第3級ブチル-4-ヒドロキシ安息香酸グリシジル、3,5-ジ第3級ブチル-4-ヒドロキシ安息香酸グリシジル、3-第3級ブチル-6-メチル-4-ヒドロキシ安息香酸グリシジル、3-第3級オクチル-5-メチル-4-ヒドロキシ安息香酸グリシジル、3-第3級ブチル-5-エチル-4-ヒドロキシ安息香酸グリシジル、2-(3-第3級ブチル-4-ヒドロキシフェニル)酢酸グリシジル、2-(3,5-ジ第3級ブチル-4-ヒドロキシフェニル)酢酸グリシジル、2-(3-第3級ブチル-6-メチル-4-ヒドロキシフェニル)酢

5

ーメチルー4ーヒドロキシフェニル)酪酸グリシ
 ジル等であり、これらの化合物はいずれも一般式：



(但し、式中 R_1 、 R_2 および n は前記一般式(I)の
 場合と同じ)で示されるカルボン酸とエピクロル
 ヒドリンとから容易に合成できるものである。

本発明のもう一つの出発物質は、前記一般式(II)
 で示される構成単位を有する重合体または共重合
 体であるが、これを具体的に例示すると、アクリ
 ル酸重合体、メタクリル酸重合体、アクリル酸/
 スチレン共重合体、アクリル酸/アクリル酸メチ
 ル共重合体、メタクリル酸/アクリル酸メチル共
 重合体、アクリル酸/酢酸ビニル共重合体、メタ
 クリル酸/酢酸ビニル共重合体、アクリル酸/エ
 チレン共重合体、メタクリル酸/エチレン共重合
 体等があげられる。なお、上述の重合体または共
 重合体は該当する単量体を公知の方法、例えばラ
 ジカル重合開始剤、光あるいは熱等により重合せ
 しめると容易に得られるし、得られた重合体また
 は共重合体の平均重合度としてはポリオレフィン
 の耐酸化効果を考慮すると1000以下が望まし
 く、これはメルカプタン等の連鎖調節剤を適量
 用いることにより容易に達成できるのである。

本発明の製造方法は、上述の二つの出発物質、
 すなわち、一般式(I)で示される化合物の少なく
 とも一種と一般式(II)で示される構成単位を有する重
 合体または共重合体とを用いて反応せしめるよう
 にするのであるが、この場合の反応条件としては、
 溶剤の非存在下または適当な溶剤例えばテトラ
 クロルエタン、ジメチルホルムアミド、ジメチル
 アセトアミド、ジメチルスルホキシド等の存在下、
 またはポリエチレン、ポリプロピレン等のポリオ
 レフィン中で、100~300℃の温度において
 加熱せしめるだけで容易に反応が進行して本発明
 の目的とする前記一般式(III)で示される構成単位を
 有するフェノール基含有付加重合体が得られるの
 である。

このようにして得られる本発明の安定剤すなわ
 ち前記一般式(III)で示される構成単位を有するフェ
 ノール基含有付加重合体は、ポリオレフィン類の
 恒久的な安定剤としての優れた性能を発現するが、

6

実際には0.01~20重量%(対ポリオレフィン)
 の濃度でポリオレフィン類を安定化せしめること
 ができるし、さらに公知のパーオキサイド分解剤
 や紫外線吸収剤等と併用すると相乗作用的にポリ
 オレフィン類の安定化を促進せしめるという特性
 をも具有しているのである。

以上述べたように、本発明の製造方法によると、
 ポリオレフィン類特にポリプロピレンの安定剤と
 して極めて有効な前記フェノール基含有付加重合
 体が簡易に得られるので、本発明の出現は斯業の
 今後の発展に大きく貢献するものである。

また、ポリオレフィン以外のポリアミド、ポリ
 塩化ビニル、アクリル樹脂、ABS樹脂、スチレ
 ン系樹脂等有機高分子化合物を安定化することも
 できる。

以下、具体的な実施例により本発明をさらに詳
 細に説明する。

なお、実施例中における部はすべて重量部の意
 である。

実施例 1

3-(3,5-ジ第3級ブチルー4-ヒドロキ
 シフェニル)プロピオン酸ナトリウム100部エ
 ピクロルヒドリン300部、テトラメチルアンモ
 ニウムアイオダイド2.6部を80℃に3時間加熱
 攪拌し、反応終了後、混合物を水洗し次いで減圧
 蒸留したところ、3-(3,5-ジ第3級ブチルー
 4-ヒドロキシフェニル)プロピオン酸グリシ
 ジル(沸点197~212/3mmHg)58部が得
 られた。

次に、上記3-(3,5-ジ第3級ブチルー4
 -ヒドロキシフェニル)プロピオン酸グリシジ
 ル33部と平均分子量5200のメタクリル酸/ス
 チレン共重合体(重量比:45/55)19部を
 ジメチルスルホキシド100部にとかし、140
 ℃で5時間反応せしめた。反応終了後、反応混合
 物を室温まで冷却し、ついで水/メタノール混合
 液を加えることによつて付加重合物を沈殿させ、
 さらに水/メタノールで洗浄し、最後に乾燥せし
 めたところ、得られた付加重合体の収量は49部
 であり、また赤外吸収スペクトルから波数910
 cm^{-1} のエポキシ基にもとづく吸収は消失し
 3500cm^{-1} の水酸基の吸収が認められ、この
 ことから、エポキシ基とカルボキシル基の付加重
 合体が生成していることが確認された。

実施例 2

平均分子量12000のアクリル酸/エチレン共重合体(重量比:10/90)7.2部と3-(3-第3級オクチル-5-メチル-4-ヒドロキシフェニル)プロピオン酸グリシジル3.5部を200℃で30分間反応させた。ついで得られた付加重合物を粉碎し、未反応のエポキシ化合物をメタノールにより抽出して除去し、残渣の赤外吸収スペクトルを測定したところ、フェニル基にもとづく吸収が認められた。

実施例 3

平均分子量4500のアクリル酸/メタクリル酸メチル共重合体(重量比:50/50)1.4部、3-(3,5-第3級ブチル-4-ヒドロキシフェニル)プロピオン酸グリシジル3.4部およびポリプロピレン粉末45.2部を混合し、220℃で20分間混練した。ついで得られた重合体からフィルムを作成し、赤外吸収スペクトルを測定したところ、波数910 cm^{-1} のエポキシ基の吸収は消失し、新たに3500 cm^{-1} の水酸基の吸収が認められ、このことからエポキシ基とカルボキシル基の付加重合体が生成していることが確認された。

(応用例)

(A): 固有粘度1.5のポリプロピレン粉末に実施例1で得られたフェノール基含有付加重合体を1.0重量%混合し、220℃で成形し、次いで270℃で溶融紡糸し、130℃で延伸して原糸を得た。さらに、この原糸をテトラクロルエ

※ チレン中、溶比1:50で32℃、20分間処理してドライクリーニング処理糸を得た。

(B): 実施例3で得られたフェノール基含有付加重合体を含有するポリプロピレン含有物をさらに未変性ポリプロピレンで10倍に希釈し、同様にして原糸およびドライクリーニング処理糸を得た。

(C): 上記安定剤の代わりに公知の安定剤"Ionol"(シエル社製:2,6-第3級ブチル-4-メチルフェノール)をポリプロピレン粉末に0.3重量%混合し、同様にして原糸およびドライクリーニング処理糸を得た。

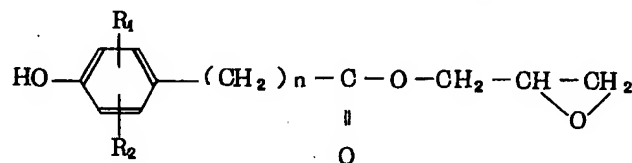
次に、これらの試料について140℃の熱風乾燥機中で加速劣化試験を行ったところ劣化開始時間(hr)について次表のような結果を得た。

試料番号	原 糸	ドライクリーニング処理糸
(A)	92	84
(B)	78	70
(C)	52	8
安定剤なし	2	2

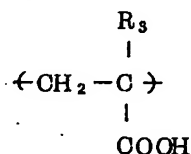
この結果よりしても、本発明の製造方法によつて得られた(A)および(B)の安定剤は従来の安定剤に比して脱落が少なく、優れた永久的安定性をポリプロピレンに与えることが明瞭に認められた。

特許請求の範囲

1 一般式:



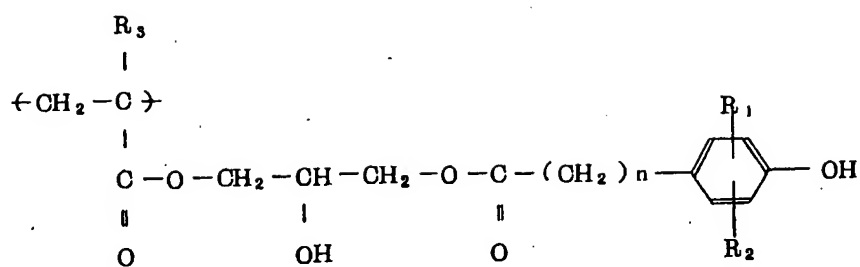
(但し、式中 R_1 , R_2 はいずれか一方が水素または両方とも炭素数1~18のアルキル基、 n は0, 1, 2, 3の整数である)で示される化合物の少なくとも一種と一般式:



(但し、式中 R_3 は水素またはメチル基である)で示される構成単位を有する重合体または共重合

9

10



(但し、式中 R_1 、 R_2 、 R_3 および n は上記一般加重合体を得ることを特徴とする安定剤の製造方式の場合と同じ)で示される構成単位を有する付10法。